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Microstructural Investigation of High Emittance Glass Coatings on Fibrous Ceramic Insulation

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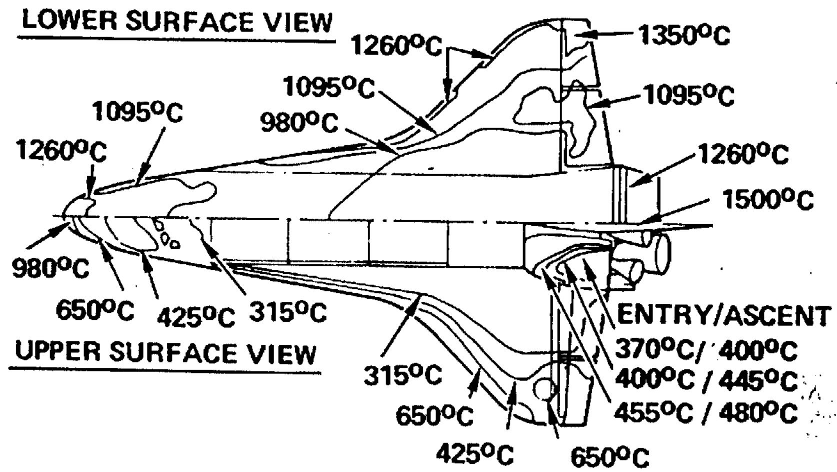
Sandia National Laboratories

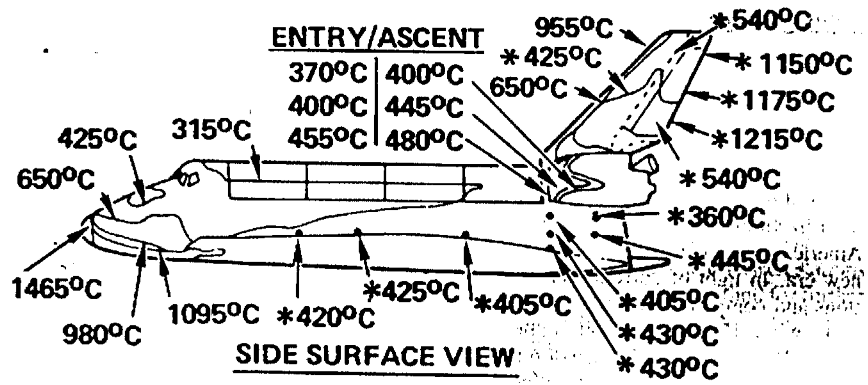
Thermal Protection Materials and Systems Branch

Outline

- Background
  - Space Shuttle Thermal Protection System (TPS)
  - Types of TPS
    - Tiles, Blankets, Leading Edges, and Coatings
- Processing
  - Tiles
  - Coatings
- Properties
  - Mechanical
    - Impact Resistance
- Microstructural Examination of Toughened Uni-Piece Fibrous Insulation (TUFI)
- Summary
- Future Work

Typical Surface Temperatures Experienced During Reentry





*DENOTES ASCENT TEMPERATURES (MAXIMUM YAW 8 DEG)

Ames Developed Thermal Protection Materials Adopted to date on Shuttle

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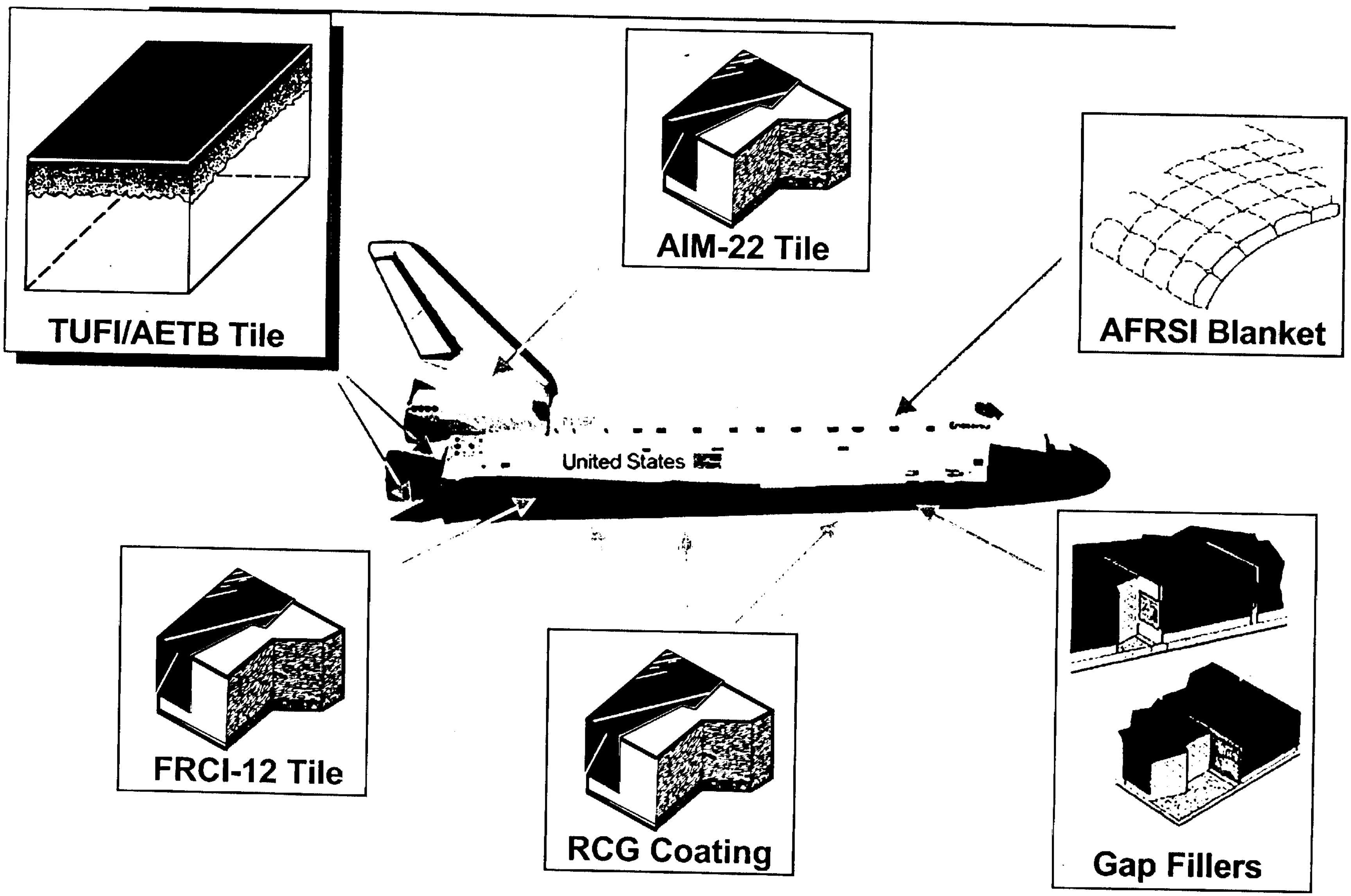


Rigid Fibrous Ceramic Tile and Coating Systems

Tile Systems

- Pure Silica
- Fibrous Refractory Composite Insulation (FRCI)
  - Silica and Aluminoborosilicate (Nextel 312) Fibers
- Alumina Enhanced Thermal Barrier (AETB)
  - Silica, Nextel 312, and Alumina Fibers

Coating Systems

- Reaction Cured Glass (RCG)
  - Borosilicate Glass and SiB_4 emittance agent
- Toughened Uni-Piece Fibrous Insulation (TUFI)
  - Borosilicate Glass, SiB_6 and $MoSi_2$

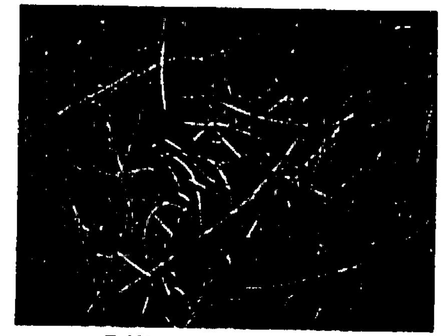
Raw Materials

Fibers

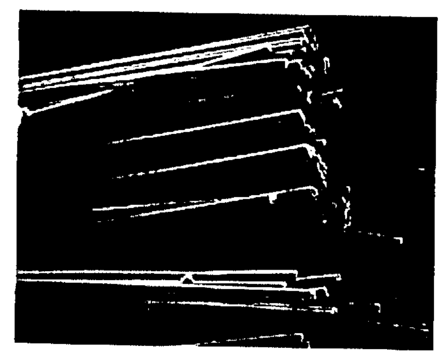
- Silica
  - 1-3 μm diameter
- Nextel 312
  - 62% Al_2O_3-14% B_2O_3-24% SiO_2
  - 8.5 μm diameter
- Alumina
  - 96% Al_2O_3-3% SiO_2
  - 1-3 μm diameter

Coatings

- Borosilicate glass
  - Porous Vycor 7930 w/ added B_2O_3
- Emissivity Agents
  - SiB_4 in RCG
  - $MoSi_2$ in TUFI

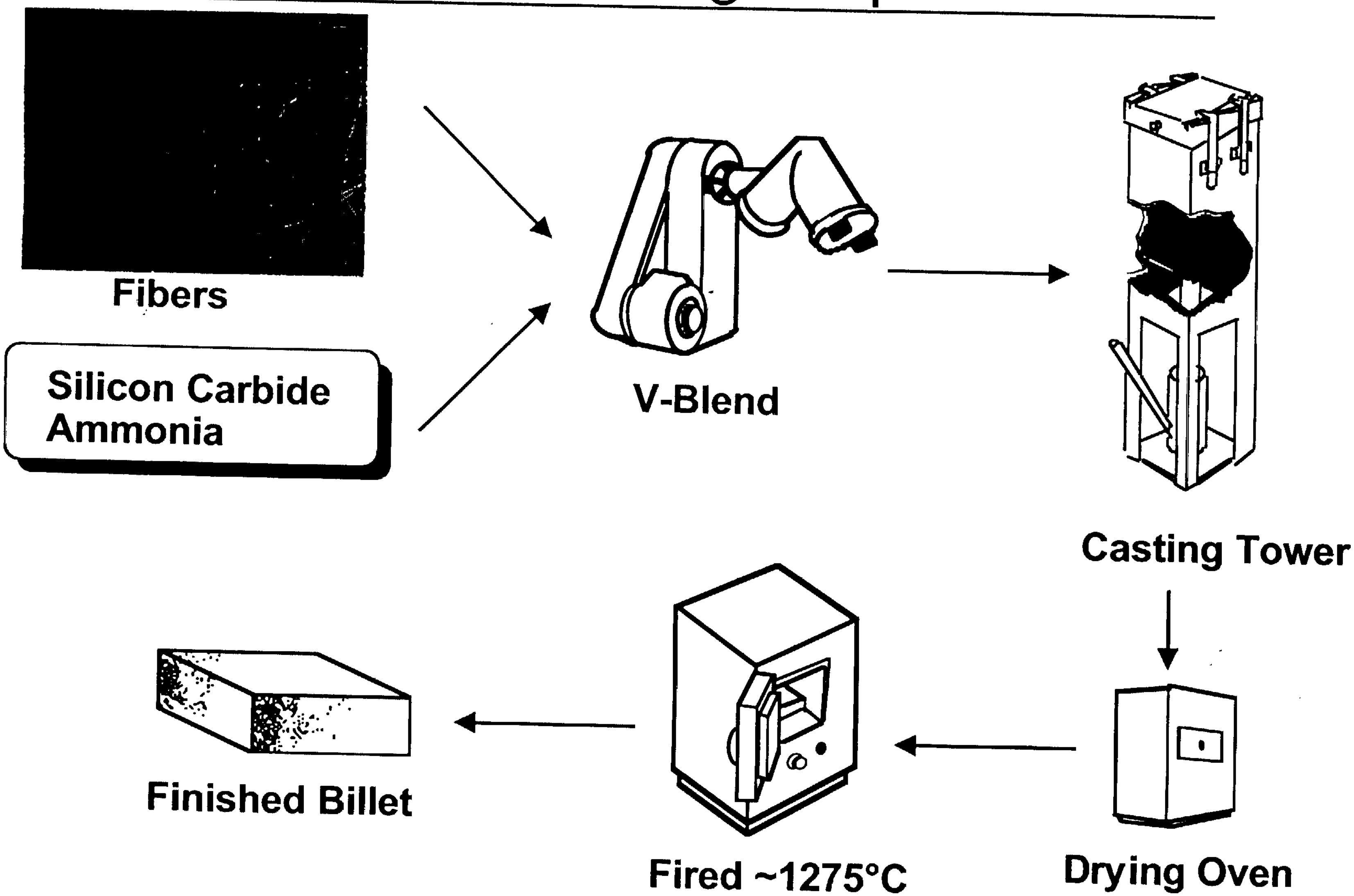


Silica Fibers



Aluminoborosilicate Fibers

Typical Tile and Coating Processing Steps



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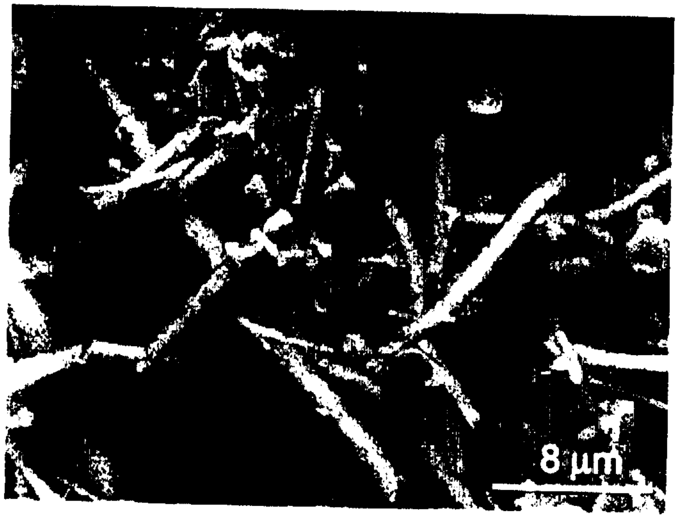
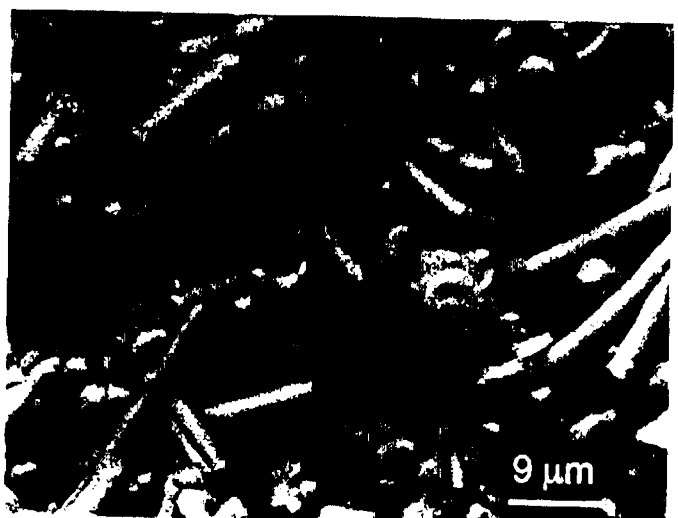
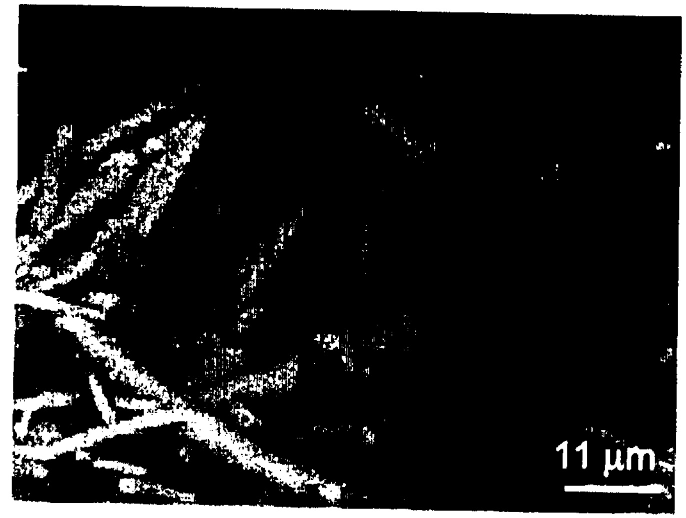
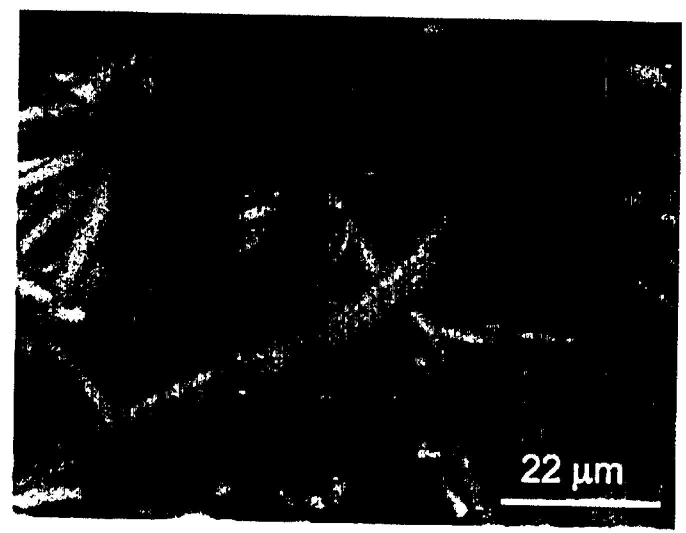
Tile Microstructures





LI-900 Pure Silica Tile





AETB Tile

Typical Coating Process

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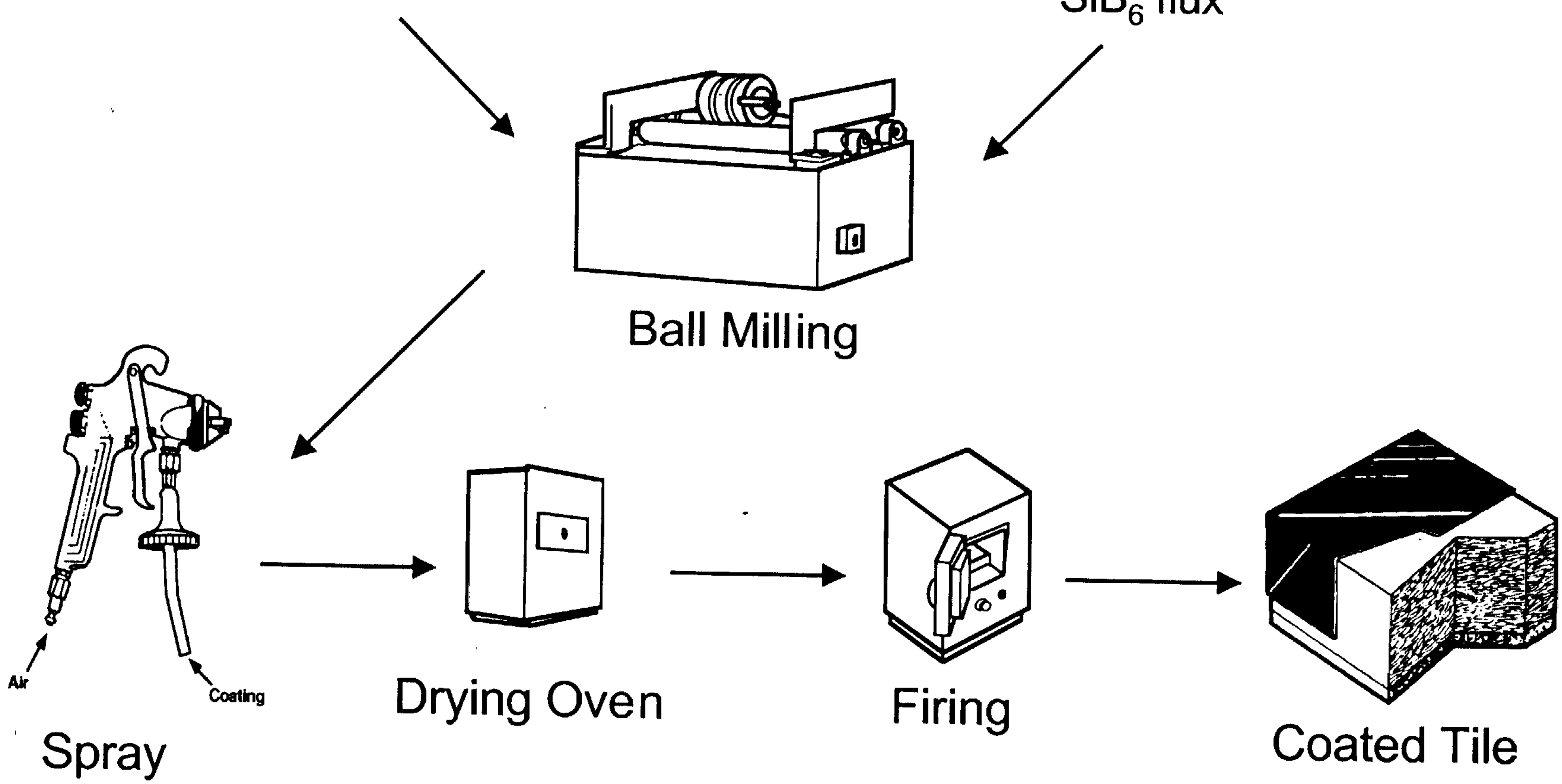
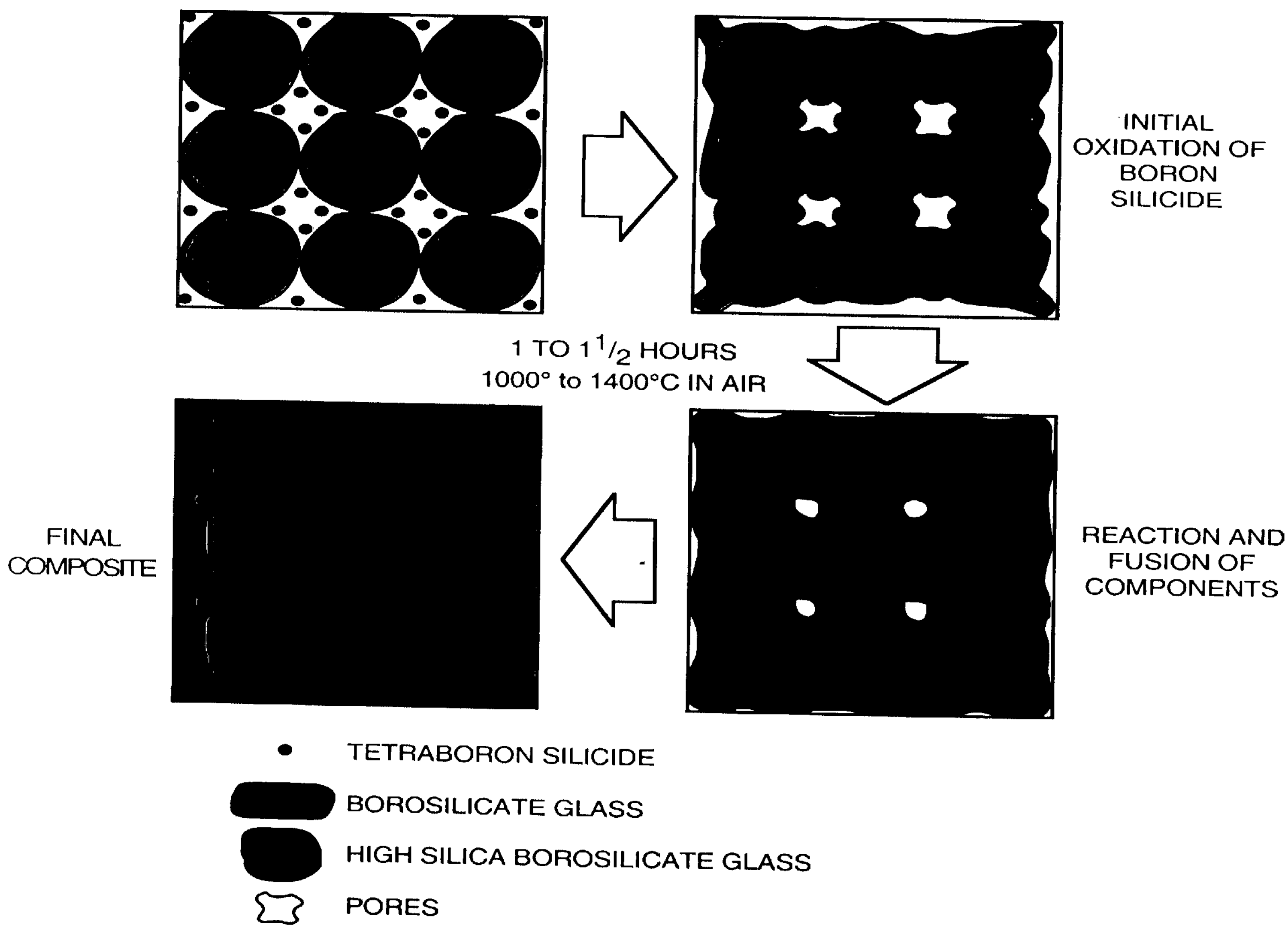
Reaction Cured Glass (RCG)
Borosilicate Glass
SiB_4 emittance agent

Toughened Uni-Piece Insulation (TUFI)
Borosilicate Glass
$MoSi_2$ emittance agent
SiB_6 flux

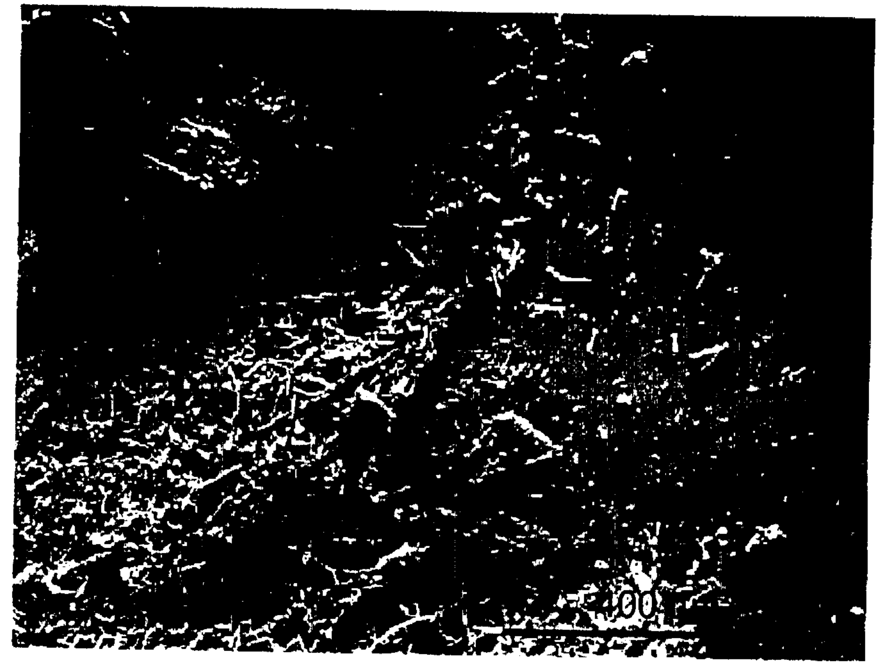


Schematic of Reaction Cured Glass



Reaction Cured Glass (RCG) Coating

- High Emittance $\varepsilon > 0.8$
- 0.38 mm thick
- Compatible with silica tiles
  - no devitrification
  - match tiles CTE
- RCG coating sits on top of tile surface
  - particle size too large to infiltrate
- Dense coating
  - initial moisture barrier
- Poor impact resistance.



Toughened Uni-Piece Fibrous Insulation (TUFI)

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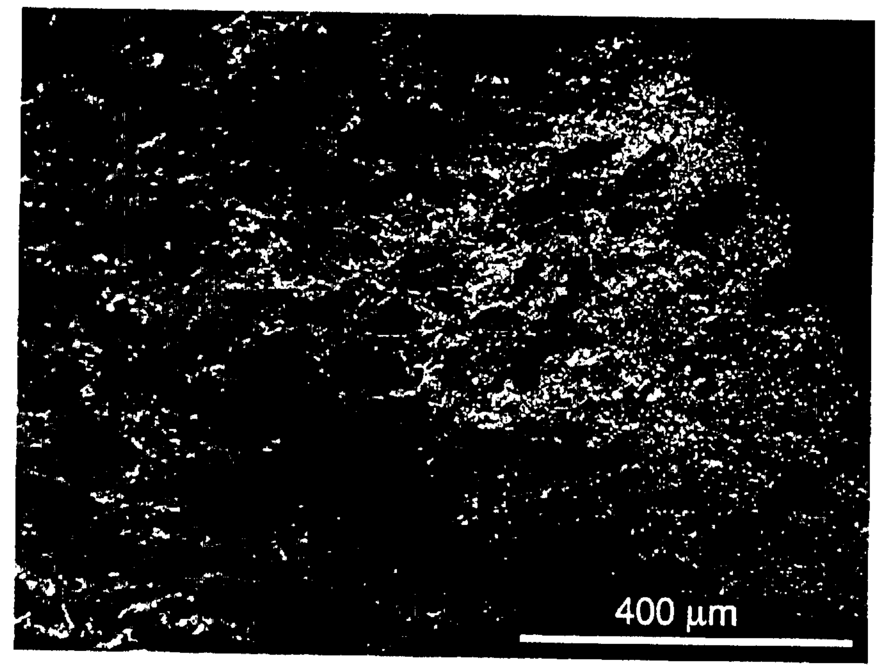
- High Emittance $\varepsilon > 0.8$
- 2.5 mm thick
- Compatible with tile
  - no devitrification
- Porous coating
- Material penetrates into the tile
  - smaller particle size



- Significantly improved impact resistance
- $MoSi_2$ act as emissivity agent
  - also increases CTE so it matches that of AETB tiles.

Microstructure of TUFI System

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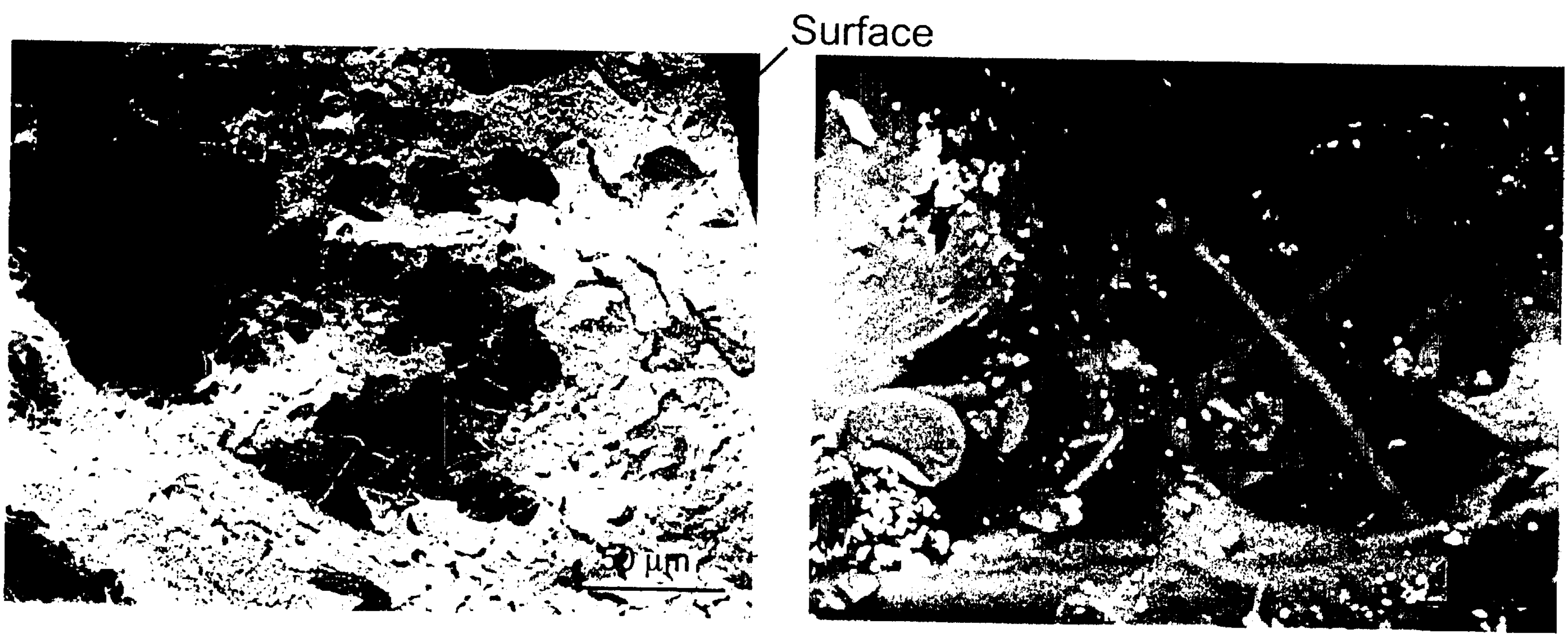

- TUFI is applied as three separate coats.
- Results in a graded coating system that is denser near the surface.
- Two scales of porosity
  - regions that appear deficient in glass
  - denser regions also have a smaller scale porosity

Comparison of Impact Resistance RCG vs TUFI

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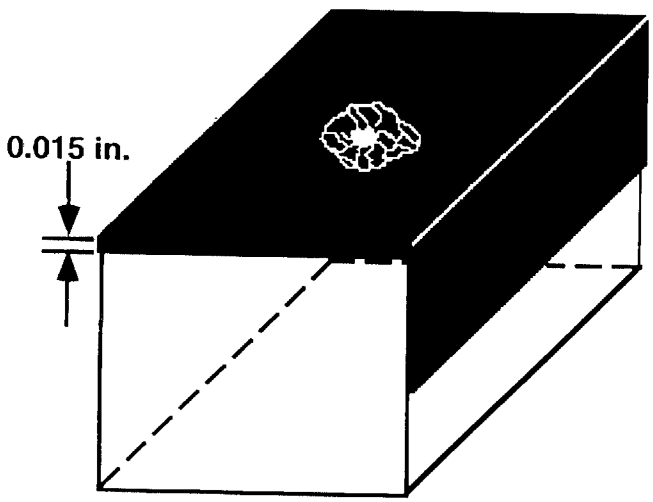
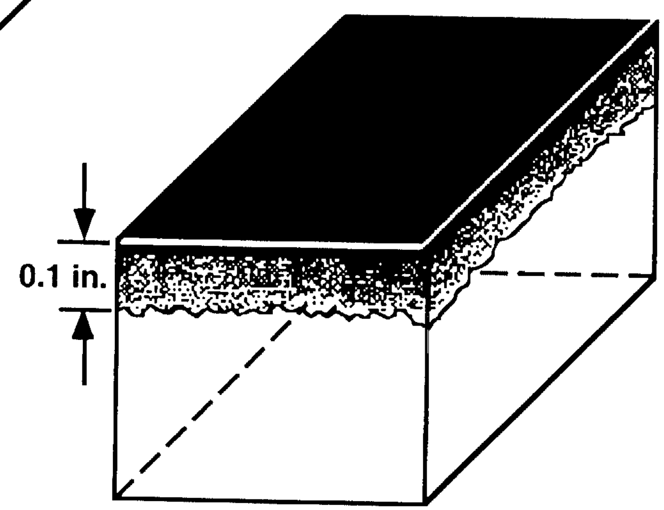
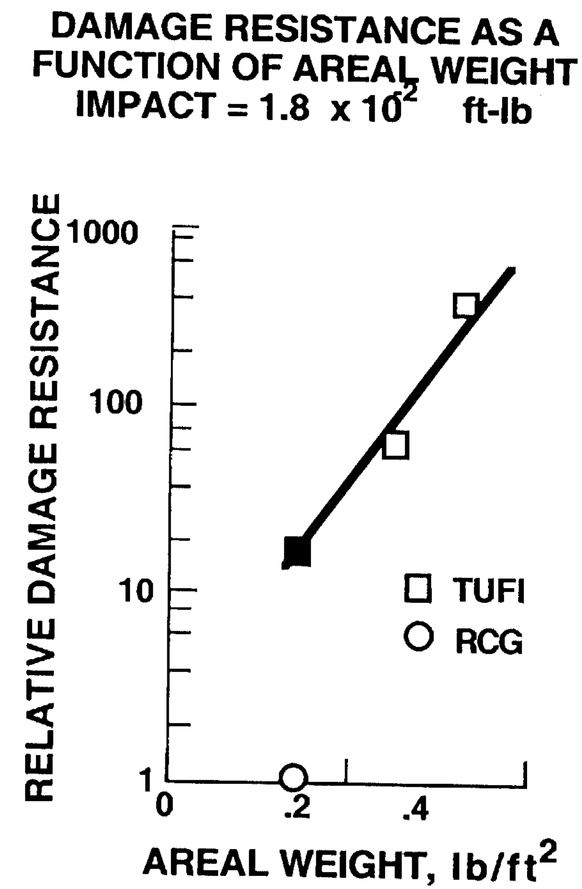
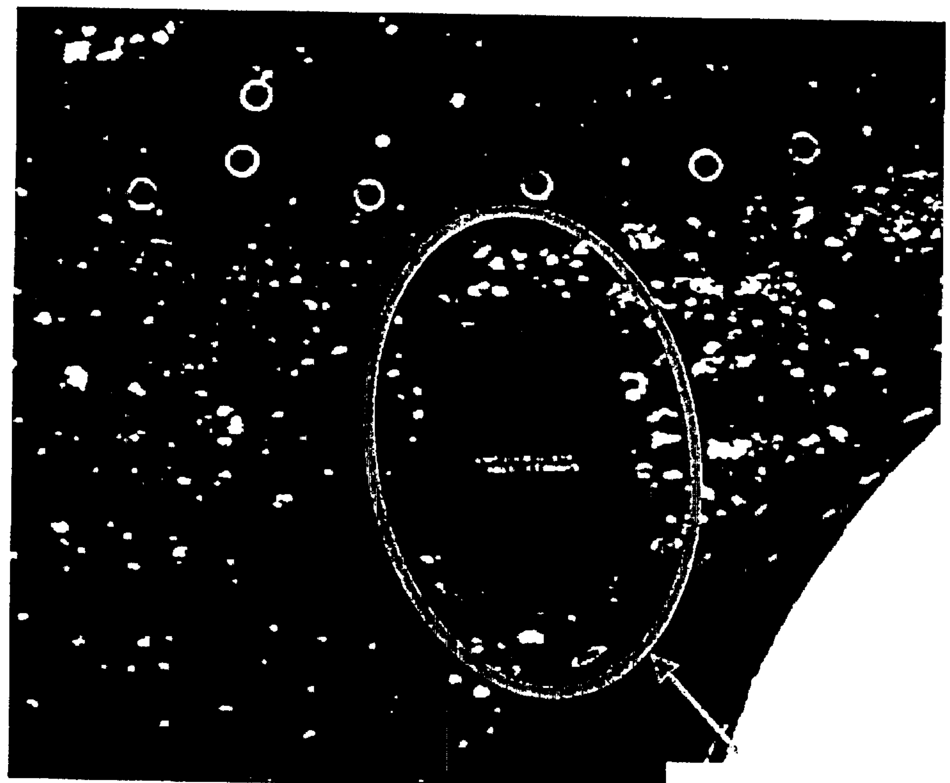






Shuttle Flight Testing of LI-900/RCG vs AETB-8/TUFI in BaseHeatshield



TUFI/AETB-8 Tiles Undamaged After Three Flights

Objective of Microstructural Investigation

- At the time RCG and TUFI were developed, analytical techniques were not available to accurately investigate the reaction mechanisms.
  - Particularly difficult to analyze for Boron.
- Future improvements in tile coatings will require fundamental understandings of these mechanisms.
- Long term consistency in current coatings will also rely on a better understanding of the current process.
  - i.e. if material vendors change, how do slight differences in starting powders affect the final coating?

Automated X-ray Spectral Image Analysis (AXSIA)

- How do you comprehensively survey the chemistry of a large area of a microstructure?

- Point analyses can be subjective– where to take them from and how many.

- 2D distributions of chemical phases are needed but simple mapping alone is not the answer. Mapping has potential artifacts and requires fore-knowledge.

'**Phase images**' are needed–a spectrum from each phase and an image describing where in the microstructure it's found

Automated X-ray Spectral Image Analysis (AXSIA)

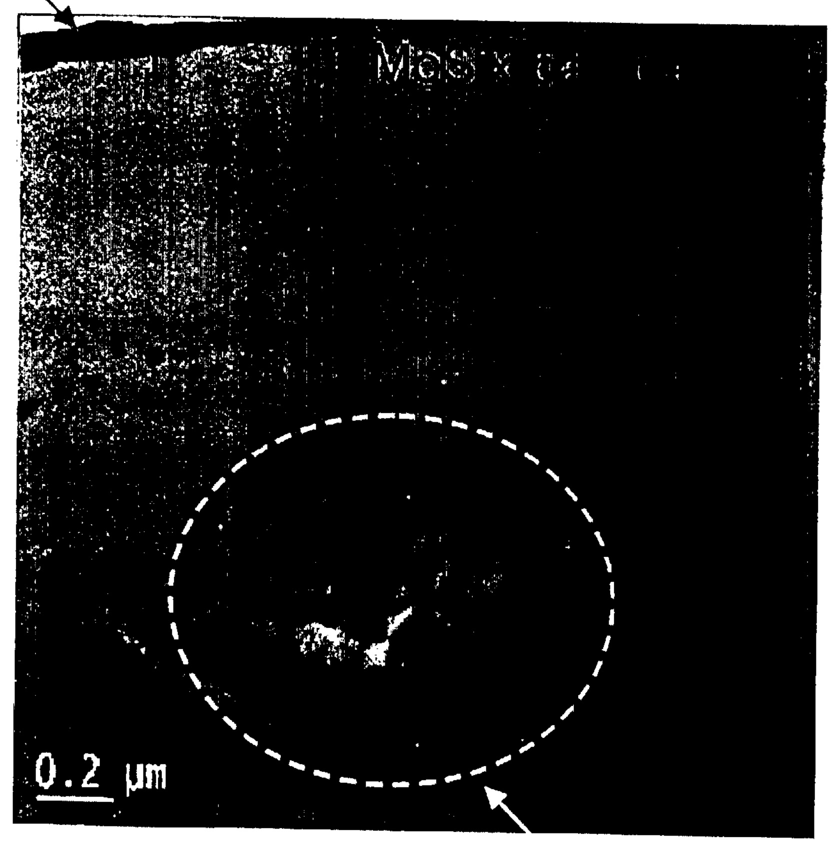
- Start off with a spectral image–a complete x-ray spectrum from each pixel in a 2D array, sampling the microstructural region of interest (hundreds of microns on a side (SEM) to nanometers on a side (TEM))

- Perform a complete statistical analysis (information extraction) on every spectrum in the spectrum image using the AXSIA software. **Analysis time** on a spectrum image with over 16,000 spectra is only **about a minute.**

- The result is a spectrum from each phase in the microstructure and an image describing that phase's location in the microstructure: 16000 spectra are reduced to a handful with no loss of chemical information

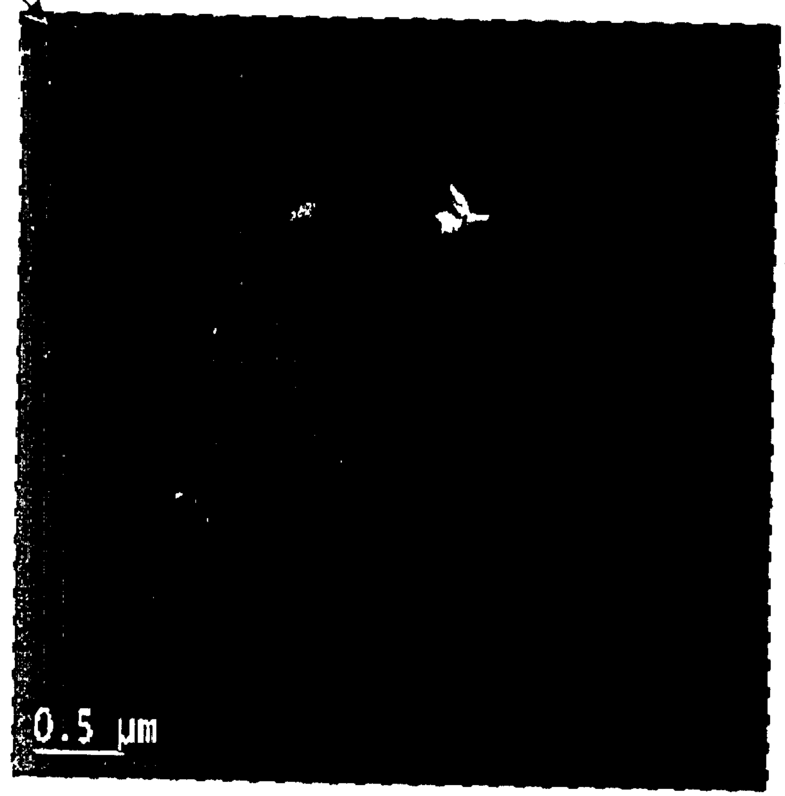
- Licensed AXSIA to Thermo NORAN, Inc., a U. S. corporation

Bright Field STEM Images of TUFI

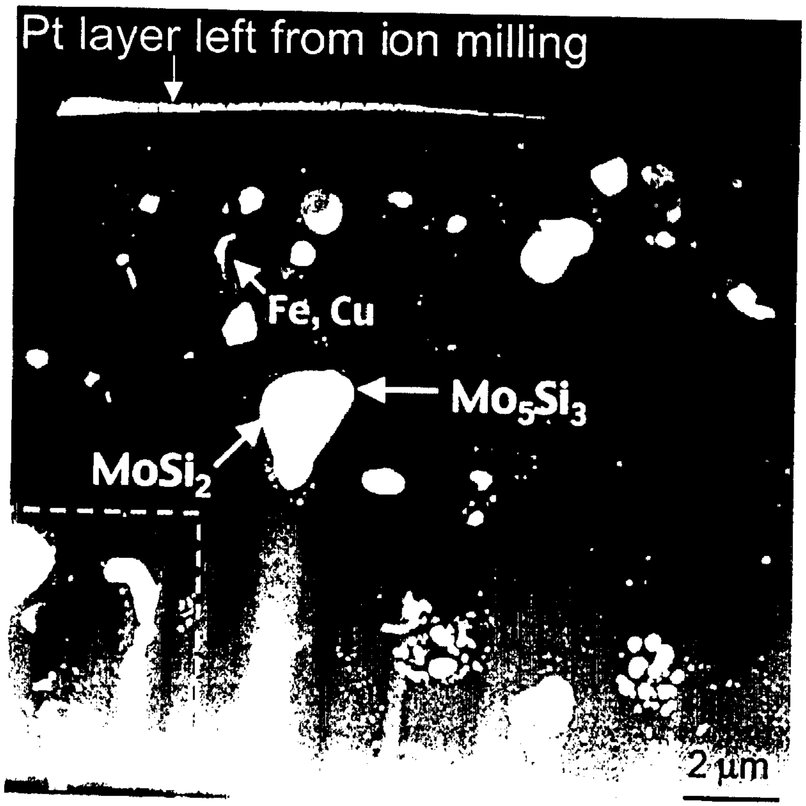


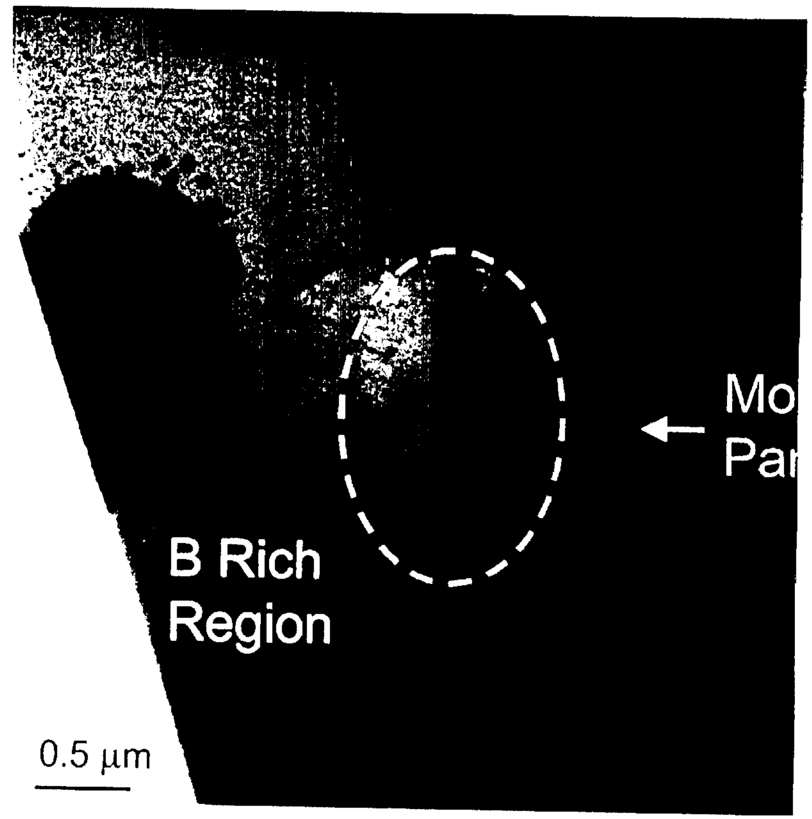
- Evidence of dissolution and reprecipitation of SiB_x and $MoSi_x$ particles.

STEM Images of TUFI Showing Distribution of Small Particles Near Surface

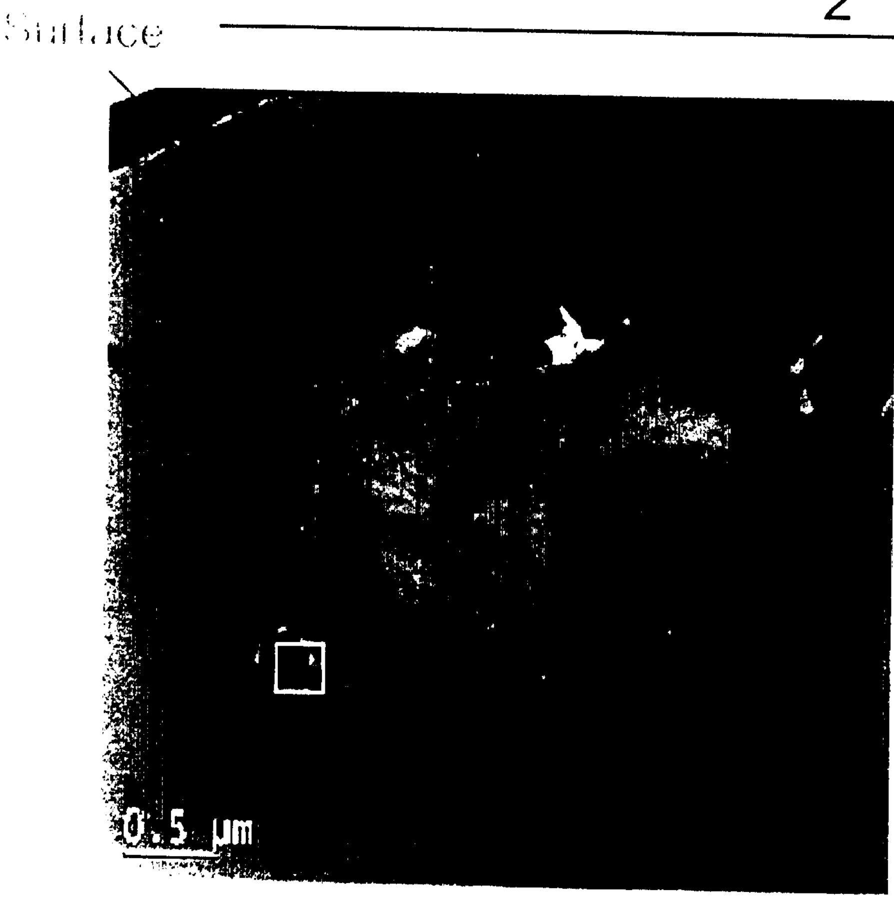


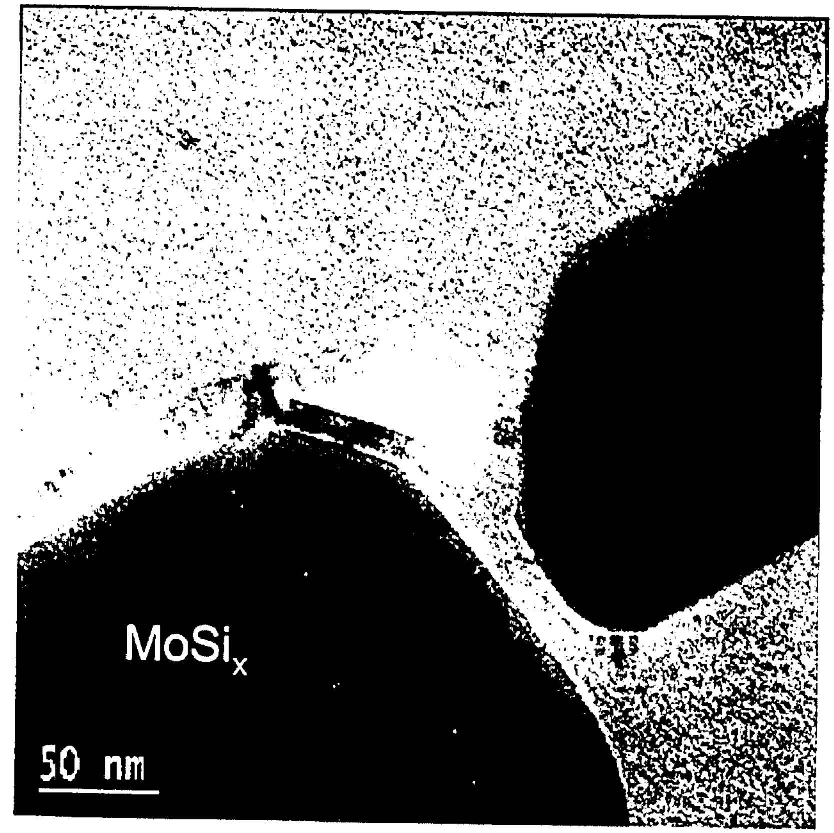
Comparison of Dark and Bright Field STEM Images





High Resolution Bright Field Image of $MoSi_2$ Particles

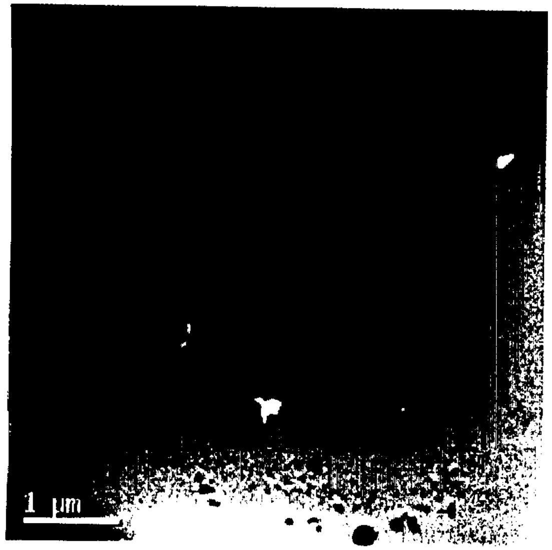


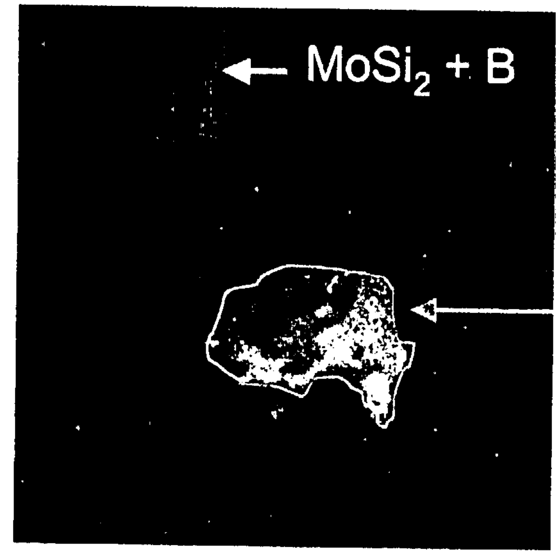


- Evidence of crystalline surface layer on $MoSi_2$ particles.

Elemental Mapping of TUFI Coating Using AXSIA

Bright Field



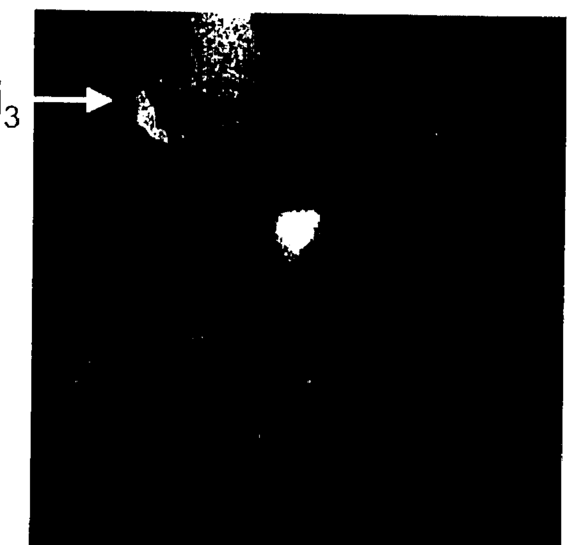


Boron Image

SiB$_x$

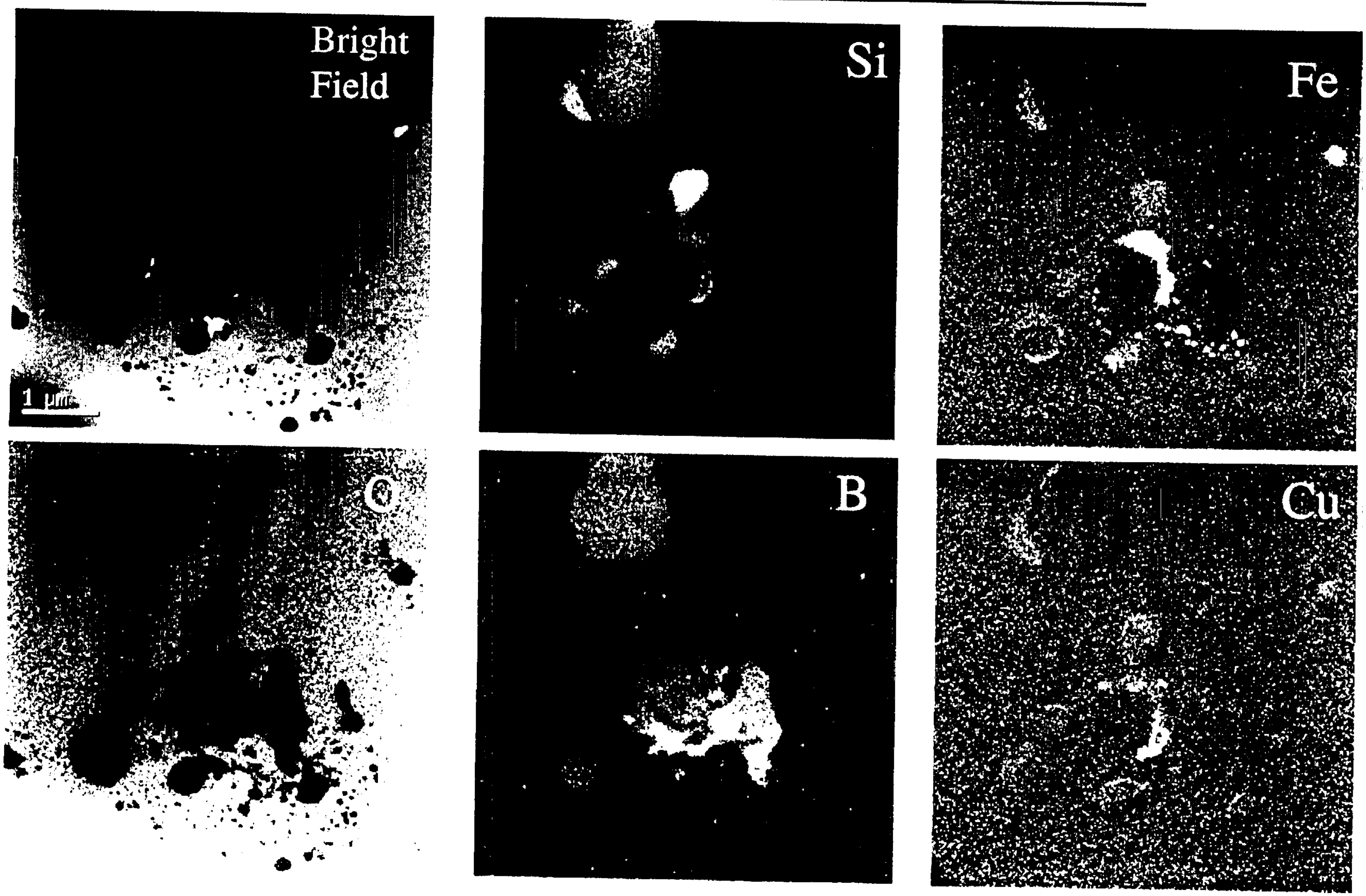
Oxygen Image

Mo$_5$Si$_3$ w/o B



Silicon Image

Elemental Mapping of TUFI Coating Using AXSIA



, surface

Summary

- Automated X-ray Spectral Image Analysis shows excellent potential for use in understanding the reactions that occur in tile coatings.
- Images reveal that the reaction mechanisms in TUFI, and presumably RCG, are complex.
- Evidence of dissolution and reprecipitation of $MoSi_2$.
- Evidence of Fe and Cu solubility in Mo_5Si_3.
- Appears to be some solubility of B in $MoSi_2$ but not in Mo_5Si_3.

Future Work

- Systematic use elemental mapping to investigate the evolution of RCG and TUFI during firing.
- Investigate the influence of SiBx on the coatings
  - SiB_4 vs SiB_6
  - Different vendors
    - How trace impurities affect coating formation
- Look for evidence of reactions at the fiber coating interface
- Look at interface between fibers
- Investigate changes in tile microstructure during use.
- Improved our understanding of the reaction mechanisms that occur in tile coatings in order to develop improved coatings for future applications.